



Effect of soils with varying degree of weathering and pH values on phosphorus sorption



V. Antoniadis^{*}, R. Koliniati, E. Efstathiou, E. Golia, S. Petropoulos

Department of Agriculture Crop Production and Rural Environment, University of Thessaly, Fytokou Street, GR-384 46, Volos, Greece

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ABSTRACT

Various soil properties are known to influence P retention, but it is not clear which of them are predominant when soils of different degree of weathering are compared, and which when newly developed soils differ mainly in activity (pH). We chose 23 typical Mediterranean low organic matter-content soils: 13 of them differed in weathering (4 Alfisols, 4 Entisols, and 5 Inceptisols), and 10 were newly developed Entisols, of which 5 were acidic and 5 alkaline. We conducted batch P sorption tests at $C_0 = 0\text{--}100 \text{ mg L}^{-1}$, measured important soil physico-chemical properties, and correlated them with sorption indices. Alfisols were significantly higher in total “free” Al and Fe, as well as in well-crystalline oxides, and this led to higher P sorption by Alfisols. Correlation analyses in the activity-divided soils revealed that amorphous oxides, although significantly higher in the acidic soils compared to the calcaric, did not have any influence in P sorption, neither did any other oxides species, while CaCO_3 , along with pH, were the important factors to enhanced P retention. Contrary to that, in the taxonomy-divided soils, neither pH nor CaCO_3 played any significant role in P sorption, which was rather influenced by oxides (mainly the amorphous, but to a lesser degree by the crystalline species as well). We conclude that oxides are the key soil property influencing P sorption among soils of different weathering (even if these soils also differ in pH and CaCO_3), while within the same taxonomic order, CaCO_3 and pH becomes the important factor.

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1. Introduction

Phosphorus, an important macro-nutrient, is usually the single most restricting element for plant production. The reason is that its readily phyto-available soil pool, the water soluble, is only a minor fraction of the total soil P, which, during high-demand seasons may be replenished many times per day, and thus needs to be recharged by other labile P pools (Nesme et al., 2014). Thus labile P species influence the levels of soil P availability, and are known to be related to certain soil properties, most important of which are pH, CaCO_3 , organic matter, and Al, Fe, and Mn oxides (Al-Rohily et al., 2013).

There are two types of studies typically employed for assessing P availability: sorption tests and the use of extractants. From such studies it has been reported that P tends to be strongly retained by soils with slightly alkaline/calcaric, as well as with acidic pH, each for different reasons. In calcaric soils, P is bound by CaCO_3 , while in acidic pH it is soil oxides that are expected to play a key role. Carbonate surfaces have a two-fold effect: They provide abundant Ca ions that cause P precipitation as insoluble Ca-P species, and directly retain P

electrostatically through the exchange of HCO_3^- for H_2PO_4^- . This becomes more effective as specific surface increases, i.e., as clay percentage increases (von Wandruszka, 2006). On the other hand, oxides retain P onto their surfaces in mono- or bi-dentate bonds. It is expected that in acidic soils, oxides ability to retain P increases, because oxide surfaces enhance their positive pH-dependent charge and also increase their reactivity (Yuji and Sparks, 2001).

As a consequence, in calcaric soils both carbonate and oxides surfaces may have a role in P retention, while in acidic soils CaCO_3 is non-existent, and it is only the oxides that will mostly influence P. However, the role of oxides in P availability becomes complicated when soils at different stages of weathering are studied, because oxides content increases with weathering, but oxides crystallinity, a factor that reduces chemical reactivity, also increases (Shi et al., 2011). Moreover, it is expected that in soils with progressed weathering, parent material-derived CaCO_3 should be diminished, and, if any exist, it should only be pedogenetic.

It is thus unclear what soil properties will influence P retention in soils with similar pedogenetic “age” but with different pH, and what in soils differing in weathering. Although there have been various studies concerning the role of oxides to P retention, such works tend to study taxonomic orders of high degree of weathering (e.g., Oxisols, Ultisols), not usually found in, and thus not directly relevant

^{*} Corresponding author.

E-mail address: vasilisrev@yahoo.com (V. Antoniadis).

to, the Mediterranean region. Also to our knowledge there is a void in the literature concerning works employing high number of soil samples (e.g., over 20), necessary for better statistical interpretation, that would compare soils divided according to pH (i.e., activity) and according to taxonomy and the degree of weathering. Thus it is important to study the role of oxides when comparing samples among (a) soils with variable degree of weathering, where the role of oxides may be more predominant, and (b) soils within the same taxonomy class, where the role of pH and CaCO_3 may be more predominant. In such a manner, it would be possible to clarify the role of soil properties in P retention within each of these soil categories. This is even more evident in areas with low organic-matter content (such as those in the Mediterranean region). Organic matter is known to affect P sorption, as was also observed by Debicka et al. (in press), who found that removal of organic matter with H_2O_2 decreased P sorption capacity and increased P desorption. In our tested soils, organic C is expected to have no significant effect.

We tested the hypothesis that in soils at different stage of pedogenetic age, P sorption will be dependent on oxides, while in recently developed soils, CaCO_3 will control P retention. Thus the aim of this work was to study P mobility in low organic matter soils, by using a series of soil extractants and batch sorption isotherms, in order to examine the role of various parameters in soils with variability in the degree of weathering and pH.

2. Materials and methods

We obtained 23 soil samples at 0–20 cm depth from Central Greece, continuously cultivated for decades. Ten of them were of the same taxonomic order (Entisols) and selected so that they may differ in activity: Five of them (soils A, B, C, D, and E) were acidic, while the rest (soils F, G, H, I, and J) were alkaline, either Xerofluvents (Fluvisols according to World Reference Base (WRB) classification (FAO, 2015), soils of xeric temperature regime, developed on fluvial materials which is being deposited more frequently than soil development process rates, thus without a B horizon) or Xerorthents (Regosols according to WRB, xeric, erosion-affected shallow soils with no B horizon). The other 13 soils represented the three major taxonomic orders of different progress in weathering typical in the Mediterranean: 4 were Entisols (all of which Xerofluvents, soils E1, E2, E3, and E4), 5 Inceptisols (Cambisols as per WRB, xeric, with intermediate level of weathering, typically with ochric epipedon and cambic B horizon, soils I1, I2, I3, I4, and I5), and 4 Alfisols (Luvisols as per WRB, the most highly weathered soils of the region, all of which Rhodoxeralfs, otherwise known as “Red Mediterranean soils” or “Terra Rossa”, soils A1, A2, A3, and A4). In the 13 taxonomy-divided soils pH was not a selection factor. Details on the exact geographical positioning, as well as the taxonomic class of the obtained samples, are presented in the supplementary material (Table S1, and a “.KML”-extension file in Google Earth background). All 23 soil samples were purposefully obtained from cultivated areas so that they may be of low organic matter. The samples were air-dried, passed through a 2-mm sieve, and analysed for selected physico-chemical properties according to Rowell (1994): pH (1:2.5 H_2O), particle size distribution (Bouyoucos hydrometer), organic C (wet oxidation), CaCO_3 (calcmeter), and cation exchange capacity (CEC, 1 M CH_3COONa). Soil oxides were also measured: total “free” Al and Fe oxides (pH-buffered dithionite-citrate-carbonate method, annotated with subscript “d” thereafter), as well as the amorphous oxides (extracted with ammonium oxalate, with subscript “o” thereafter). From the difference of the two, we estimated the well-crystalline, with subscript “d-o” thereafter. We also conducted four P extractions: Water soluble (10 mM CaCl_2 , thereafter WS-P), ammonium oxalate (AO-P), Mehlich-3 (M3-P), and Olsen (with 0.5 M NaHCO_3 , Olsen-P). We also calculated phosphorus saturation index (PSI) as the fraction of AO-P over the sum of Alo and Feo (all units in mmol kg^{-1}). Then we conducted batch sorption tests at 1-to-10 soil-to-solution ratio with added phosphorus concentrations

of $C_0 = 1\text{--}100 \text{ mg L}^{-1}$. We measured P sorption, q , and P in the equilibrium solution, C , and we fitted the experimental data to the Freundlich and Langmuir isotherms, as follows:

$$q = K_F C^N \text{ (Freundlich), linearized as } \log q = \log K_F + N \log C, \text{ and}$$

$$q = q_{\max} K_L C / (1 + K_L C) \text{ (Langmuir), linearized according to Lineweaver–Burk as } 1/q = (1/q_{\max} K_L) (1/C) + 1/q_{\max},$$

where K_F , N , q_{\max} and K_L are constants, with the latter two related to maximum sorption capacity and bonding strength, respectively.

In order to assess the goodness of fitness, we used R^2 (the closer to unity the better the fitness) and an error function (the lower the value, the better the fitness): Derivative of Marquardt’s Percent Standard Deviation (MPSD, as per Foo and Hameed, 2010). From the fitted isotherms we calculated the distribution or partitioning coefficient (K_d), averaged over the whole range of added P concentration. This sorption index, along with q_{100} (measured sorption at $C_0 = 100 \text{ mg L}^{-1}$) and q_{\max} (derived from Langmuir) were used in this work for studying P.

We then performed regression analyses between soil properties versus P extractability and P sorption indices. Also average values in various soil divisions were compared for their significance at the level of $p < 0.05$ with ANOVA. All such analyses were conducted with the use of the statistical package Statgraphics. We present the above mentioned parameters of soil properties, P extractability, and soil oxides content, and P sorption isotherm parameters, and statistically compare them as averaged for the various studied soil divisions, but we also include the data per soil Tables S2–S4 (supplementary material).

3. Results

Soil properties did not differ among soil orders in the taxonomy-divided soils, except for clay and CEC, which were significantly higher in Alfisols. In the activity-divided soils, pH and CaCO_3 were significantly higher in the alkaline soils, as was also the case with organic C. Acidic soils also extracted higher Olsen-P and M3-P levels than the alkaline (Table 1).

Although the percentage of amorphous-over-total free Al oxides was higher in Entisols, amorphous oxides were not different among soil orders (Table 2). As for total free dithionite-extracted oxides, they were higher in Alfisols. Phosphorus saturation index, indicating P retained onto chemically reactive oxides, did not differ in any of the three soil orders, a reflection of the similar levels of AO-P, Alo and Feo across soil orders, and neither did it differ in the activity-divided soils.

Phosphorus sorption (Fig. 1, where for better comparison x- and y-axis dimensions were kept the same for all graphs), was rather higher in Alfisols (Fig. 1c) than in Entisols (Fig. 1b). This trend was also confirmed by the sorption parameters calculated with Freundlich and Langmuir (Table 3). Freundlich-calculated K_d was indeed higher in Alfisols, but q_{\max} and q_{100} were not different. Both isotherm models were good in predicting P sorption (as indicated by R^2 values approaching unity), but the MPSD error function revealed that Freundlich had lower error values.

In the taxonomy-divided soils, K_d was significantly and positively correlated with clay ($R^2 = 0.71$, $p = 0.0003$) and CEC ($R^2 = 0.83$, $p < 0.0000$), and negatively (indicating a reversely proportional relationship) with sand ($R^2 = -0.46$, $p = 0.0104$). q_{100} was negatively correlated with WS-P ($R^2 = -0.46$, $p = 0.0109$), while q_{\max} increased with Olsen-P and M3-P (Table 4). In the pH-divided soils, q_{100} and K_d increased with CaCO_3 and with pH, while they decreased with enhanced M3-P levels.

In the taxonomy-divided soils, both Al and Fe amorphous oxides influenced P sorption as indicated by K_d ($R^2 = 0.52$, $p = 0.0053$ for Alo and $R^2 = 0.36$, $p = 0.0304$ for Feo), while no such influence was observed in the pH-divided soils (Table 5). Total free dithionite-extracted Al and Fe oxides generated significant relationship with K_d ,

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